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Me₃AlNH₃ Formation and Pyrolytic Methane Loss: Thermodynamics, Kinetics and Mechanism

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The thermodynamics, kinetics, and mechanism of the reactions $\text{Me}_3\text{Al} + \text{NH}_3 \rightleftharpoons \text{Me}_3\text{AlNH}_3$ and $(\text{Me}_2\text{AlNH}_2)_3 + \text{CH}_4$ in homogeneous solution were investigated by solution calorimetry, DSC, and ¹H NMR rate measurements. The enthalpy for complex formation from NH₃ and monomeric Me₃Al in benzene was -93 kJ/mole. The observed ΔH for methane loss from the complex was 82.2 kJ/mole. Methane loss from Me₃AlNH₃ was catalyzed by excess Me₃Al monomer or monomeric Me₂AlNH₂ in equilibrium with (Me₂AlNH₂)₂ and (Me₂AlNH₂)₃. A mechanism for the (Me₂AlNH₂)₂ catalyzed reaction involving formation of the methyl-bridged intermediate (μ-Me)(Me₂AlNH₂)(Me₂AlNH₃), and subsequent loss of CH₄ by proton transfer was proposed. The enthalpy of activation for the autocatalytic reaction was 92.8 kJ/mole. A deuterium isotope effect of 8.8 was measured for this reaction. A similar mechanism was proposed for the Me₃Al catalyzed reaction, involving formation of an analogous methyl-bridged species (μ-Me)(Me₃Al)(Me₂AlNH₃) which apparently loses CH₄ and closes to metastable (μ-NH₂)(μ-Me)Al₂Me₄. This slowly disproportionates to (Me₃Al)₂ and Me₂AlNH₂; the autocatalytic path is thus slowed. ΔH for the Me₃Al-catalyzed pathway was 113 kJ/mole. The deuterium isotope effect was 5.5.

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by

Frederick C. Sauls, Leonard V. Interrante, and Zhiping Jiang

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**Me₃AlNH₃ Formation and Pyrolytic Methane Loss;
Thermodynamics, Kinetics and Mechanism**

Frederick C. Sauls,^{*, 1a} Leonard V. Interrante,^{*, 1b}
and Zhiping Jiang^{1b}

Abstract

The thermodynamics, kinetics, and mechanism of the reactions
 $\text{Me}_3\text{Al} + \text{NH}_3 \rightarrow \text{Me}_3\text{AlNH}_3 \xrightarrow{\Delta} 1/3 (\text{Me}_2\text{AlNH}_2)_3 + \text{CH}_4$ in homogeneous
solution were investigated by solution calorimetry, DSC, and ¹H NMR
rate measurements. The enthalpy for complex formation from NH₃ and
monomeric Me₃Al in benzene was -93 kJ/mole. The observed ΔH for
methane loss from the complex was -82.2 kJ/mole. Methane loss from
Me₃AlNH₃ was catalyzed by excess Me₃Al monomer or monomeric Me₂AlNH₂
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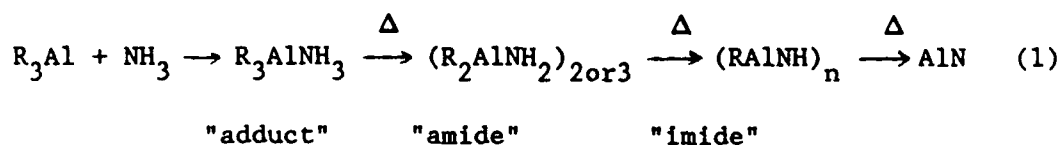
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autocatalytic path is thus slowed. ΔH^\ddagger for the Me_3Al -catalyzed pathway was 113 kJ/mole. The deuterium isotope effect was 5.5.

Introduction

A general route to nonoxide ceramic materials is the pyrolytic decomposition of a suitable organometallic precursor. While this approach has received considerable attention, the mechanisms of the underlying organometallic thermal elimination reactions have not. The elucidation of these reactions may prove important for the optimization of such ceramic generation processes; it is also essential for a full fundamental understanding of the chemistry of the inorganic compounds and polymers used in these processes.

Organoaluminum compounds are known to form adducts with ammonia, which undergo the the following series of reactions first elucidated by Wiberg in 1939:²

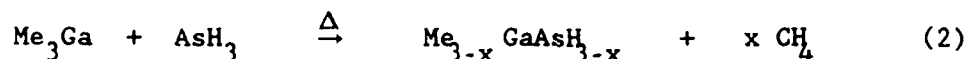


The final product AlN is a ceramic with attractive properties for electronic and structural applications.³⁻⁸

The nature of some of the amide and imide intermediates in the thermolytic conversion have subsequently been investigated and the results summarized.⁹⁻¹⁴ Thermolysis of these amides or the adduct Me_3AlNH_3 in the absence of excess ammonia yields a black powder high in carbon; however, empirical modifications of this chemistry have yielded high purity AlN.¹⁵⁻¹⁸ An understanding of the decomposition mechanism would allow rational selection of substituents on Al and N;

moreover, processing conditions to produce films or powders of appropriate purity and morphology, or compatible with on-chip device fabrication, might be selected.

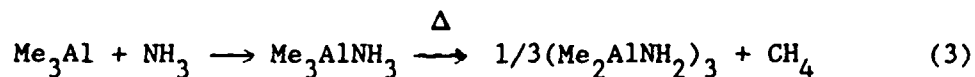
There have been few relevant kinetic studies of elimination from analogous compounds. Schleyer and Ring^{19,20} studied the pyrolysis of $\text{Me}_3\text{Ga} + \text{AsH}_3$ and $\text{Me}_3\text{Ga} + \text{PH}_3$. Their work was done in the vapor phase at reduced pressures, and focused on the surface-catalyzed decomposition to GaAs or GaP,



They found no evidence for formation of $\text{Me}_3\text{GaAsH}_3$ or Me_3GaPH_3 . The reaction could not be separated cleanly into steps, as can the $\text{Me}_3\text{Al} + \text{NH}_3$ reaction sequence. Their rate data indicate that loss of the first methane was catalyzed by the $\text{Me}_{3-x}\text{GaAsH}_{3-x}$ surface produced.

Beachley and co-workers studied the H_2 -elimination kinetics in mixtures of $(\text{Me}_2\text{AlH})_3$ with N-methylaniline, benzylamine, or methylphenylphosphine.²¹⁻²³ The processes appear to be complex, especially in the last system.

This paper reports the results of our study of the reactions



We chose trimethylaluminum because the chemistry of the system has been investigated.¹⁷ The NMR spectra are simple and the resonances of interest are well separated, affording a convenient method of following the reaction. Moreover, trimethylaluminum cannot decompose via alkene loss to the corresponding aluminum hydride,

avoiding a potential complication.

The reactivity of alkylaluminum compounds and their amine derivatives toward polar solvents, and the very limited solubility of the amine derivatives in alkanes, limit these studies to use of the neat compounds or to solutions in aromatic solvents, e. g. benzene and toluene.

Experimental

All solution preparation and handling of alkylaluminum compounds was done in a N_2 -filled drybox or in Schlenk glassware under N_2 , respecting their sensitivity to oxygen and moisture.^{24,25}

$(Me_3Al)_2$ and $(Et_3Al)_2$ (Texas Alkyls), $(Me_3Al)_2$ (electronic grade, Alfa Inorganics), ND_3 (99.5% D, Cambridge Isotope Laboratories), NH_3 (electronic grade, Matheson), D_6 -benzene, and D_8 -toluene (99.5%, and 99% D respectively, Aldrich) were used as received. NH_3 (USS AgriChemicals) was dried over Na before use. NH_2Me (Matheson) was dried by passage over KOH. Pentane (Fisher) was distilled from CaH_2 under N_2 ; benzene and toluene (Fisher) were distilled from Na under N_2 .

Me_3AlNH_3 was prepared by bubbling NH_3 for 3 hours through a solution of 25 mL $(Me_3Al)_2$ and 75 mL pentane in a dry ice/isopropanol bath. Pentane and excess NH_3 were removed in vacuo at room temperature overnight. The white solid was stored at $-30^\circ C$, as it decomposes in a few days at room temperature. NMR measurements indicate the presence of ca. 5% $(Me_2AlNH_2)_3$ in the resulting product. Me_3AlND_3 was prepared in identical fashion from ND_3 , 2 mL $(Me_3Al)_2$ and 6 mL pentane; it contained ca. 2% $(Me_2AlND_2)_3$. High purity Me_3AlNH_3 was prepared by condensing electronic-grade NH_3 into electronic-grade

$(\text{Me}_3\text{Al})_2$ with stirring for several hours at -78°C , then removing the excess NH_3 under vacuum at -78°C . This material contained no $(\text{Me}_2\text{AlNH}_2)_3$ detectable by ^1H NMR. Kinetic results reported here were obtained using the high purity product. However, allowing for the $(\text{Me}_2\text{AlNH}_2)_3$ present in the first preparation, no difference in the kinetic properties of Me_3AlNH_3 prepared by the two methods was detected. This suggests that any trace impurities present are probably not kinetically significant. $(\text{Me}_2\text{AlNH}_2)_3$ ¹⁷, $[\text{Me}_2\text{AlNHMe}]_3$ ¹⁸, and $[\text{Et}_2\text{AlNH}_2]_3$ ¹⁷ were prepared as described.

Calorimetric measurements were made in the drybox, using a Parr Model 1451 Solution Calorimeter, calibrated as recommended by the manufacturer.²⁶ The heat capacity of benzene was taken to be $1.73 \text{ J/g}^\circ\text{C}$.²⁷ Trimethylaluminum (ca. 0.5 g, 3.5 mmole) was added to weighed amounts (ca. 85 g) of benzene in the calorimeter Dewar flask, and thermal equilibration was allowed. (All weighings were carried out to the nearest milligram.) Sodium-dried NH_3 was then passed into the solution at approximately 10 mL/min. Exothermic complexation caused a linear (Slope A) temperature rise. The extent of this rise was used to compute the heat of reaction. When the reaction was complete, a sharp transition to lesser slope (Slope B) occurred, due to exothermic solution of NH_3 in benzene. The heat of solution of NH_3 in benzene (which does not appear to have been reported)²⁸ was obtained as the product of the heat of reaction and (Slope B / Slope A). The temperature eventually leveled and showed a decrease after the solution became saturated with NH_3 and escaping bubbles removed benzene vapor. Runs without trimethylaluminum showed identical behavior, without the initial slope due to the complexation reaction.

Differential scanning calorimetry was performed on a Perkin-Elmer

7 Series Thermal Analysis System. Me_3AlNH_3 was analyzed in a sealed stainless steel pan by heating from ambient temperature at $2.0^\circ\text{C}/\text{min}$.

Activation energy and reaction order were determined from the relationship²⁹:

$$k = (dH/dt)(m_o/H_o)m^x \quad (4)$$

where k = rate constant, dH/dt = heat flow rate, m_o = original sample mass, H_o = total heat flow, m = mass of unreacted sample, and x = reaction order. A plot of $\ln k$ vs. $1/T$ gave the activation energy.

^1H NMR measurements were made on a Varian XL-200 magnetic resonance spectrometer at 200 MHz, using residual protons in deuterobenzene ($\delta = 7.15$ ppm) or residual α -protons in deuterotoluene ($\delta = 2.09$ ppm) as reference. TMS was not added to the samples, as its resonance overlaps other peaks of interest. T_1 values for the methyl protons of Me_3AlNH_3 and $(\text{Me}_2\text{AlNH}_2)_3$ were 0.1 s in 0.1 M solution at room temperature. (At higher temperatures decomposition causes the concentrations to vary with time, making T_1 determinations difficult.)

An interpulse delay of 3 seconds was used at all temperatures in order to assure accurate quantitation. Several kinetics runs were repeated using 1 s delays in order to test the validity of this procedure; no change in the kinetic results were noted. All reported results were obtained using the 3 s delay.

Solutions of alkylaluminum compounds for kinetics runs were prepared gravimetrically in D_6 -benzene with initial concentrations of 0.02 to 0.5 M. Lower concentrations gave inadequate S/N for acceptable quantitation; higher concentrations generated excessive methane pressure when decomposed within the NMR tube.

For all solutions except those containing excess $(\text{Me}_3\text{Al})_2$ the kinetic runs were performed as follows. Solutions of varying initial $[\text{Me}_3\text{AlNH}_3]$ and $[(\text{Me}_2\text{AlNH}_2)_3]$ in D_6 -benzene were prepared and their decompositions according to reaction (3) were followed by ^1H NMR at 61.5°C . The area of the peak due to the methyl group of reactant Me_3AlNH_3 (B) and that of the product $(\text{Me}_2\text{AlNH}_2)_3$ (D), as shown in Figure 1, were measured. Some samples were followed to greater than 95% decomposition. The fraction of reactant remaining was computed as $\text{Fr} = \text{B}/(\text{B} + 1.5 \text{ D})$.

Series in which the ammonia concentration was varied were prepared by weighing the aluminum compound into the solvent and dividing the solution into two portions. One portion was saturated with ammonia (ca. 2 M). Mixing these solutions in different proportions produced a series with a constant alkylaluminum concentration but varying ammonia concentrations. Integration of the Al-methyl and N-H regions of the NMR spectra allowed their ratio to be computed. The width of the N-H peaks rendered integration inaccurate; the resulting uncertainty in $[\text{NH}_3]$ contributes to the scatter in Figure 7. Kinetics runs on these solutions were performed as above in random order to minimize the effect of any ammonia loss.

In the presence of excess $(\text{Me}_3\text{Al})_2$ the reaction rate cannot be followed by integration of reactant and product peaks, as a metastable compound forms which has a resonance overlapping that of the adduct. The initial rate of reaction was determined as follows. A series of solutions containing 0.081 M Me_3AlNH_3 and varying amounts of $(\text{Me}_3\text{Al})_2$ were prepared and decomposed at 55°C . The initial rate of decomposition for each solution was followed by measuring the heights of the sharp CH_4 product peak and the residual solvent proton peak, as

internal standard, at various times. (Accurate integration was not possible due to overlap of the CH_4 by the broad N-H resonance). The initial rate of decomposition was then proportional to the initial slope of the $\text{I}(\text{CH}_4)/\text{I}(\text{benzene})$ vs. time plot. The unknown concentration of residual protonated benzene used as internal standard prevents any direct comparison of the relative rates obtained using this technique with those determined using the previous method. Therefore, the relative rate of initial methane loss from a sample containing no excess $(\text{Me}_3\text{Al})_2$ was determined by an identical procedure for comparison purposes (the initial point in Figure 9).

The rate of CH_3D loss from the deuterated adduct in the presence of excess $(\text{Me}_3\text{Al})_2$ was determined by similarly following the decomposition, allowing for the difference in product (CH_4 gives a singlet, 4H; CH_3D a 1:1:1 triplet, 3H). Any NOE due to the deuterium lock irradiation would cause a relative increase in the CH_3D signal. T_1 for CH_3D would be expected to be less than T_1 for CH_4 , also tending to increase the CH_3D signal relative to that of CH_4 . Thus errors from these sources would decrease R_H/R_D and lead to an underestimate of the isotope effect.

As only the initial part of the reaction is monitored, the $[\text{CH}_4]$ in solution is well below saturation and bubbles do not form. Variations in field homogeneity will affect the peak height of both methane and the internal standard similarly; errors due to this source should largely cancel. Equilibration between solution and gas may be incomplete, and is probably the cause of much of the scatter in Figure 9. Although the relative rate measurements obtained using this method are clearly less precise than those obtained by integrating product and reactant peaks, they are sufficiently accurate for the purposes

required.

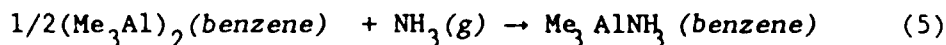
Temperatures were measured before and after each kinetics run by inserting a sealed methanol or ethylene glycol sample into the spectrometer probe, allowing thermal equilibration, and measuring the peak separation. An internal program computed the temperature using van Geet's equations.³⁰ The average of the two determinations, which differed less than 0.5 °C, was taken to be the sample temperature. For each series of kinetics runs the temperatures were varied in random fashion over the range of interest (35 - 80 °C).

Results and Discussion

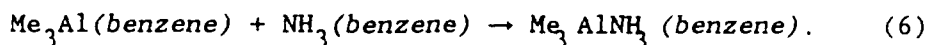
Our principal conclusions on the reactions of Me_3AlNH_3 in aromatic solvents are summarized in Scheme 1. The data supporting our conclusions will be discussed in sections labelled according to the numbers in Scheme 1.

Scheme I

A. Adduct Formation (1). When NH_3 is passed into $(\text{Me}_3\text{Al})_2$, either neat or in solution, Me_3AlNH_3 is rapidly formed. Our experimental values for the heat of solution of ammonia in benzene and for the reaction



are -12 ± 4 and -72 ± 3 kJ/mole, respectively. The heat of dissociation of $(\text{Me}_3\text{Al})_2$ in hexadecane solution³¹ and the estimated value of the heat of complexation of Me_3Al monomer with benzene³² in hexadecane are 81.2 ± 1.3 and -8 kJ/mole, respectively. Combining these values gives $\Delta H = -93 \pm 5$ kJ/mole for the coordination reaction



Henrickson *et al.*³³ have determined $\Delta H = -115.3$ kJ/mole for the same reaction in hexane, but it is unclear whether the product remained in solution or precipitated as the solid.

B. Adduct Interactions with Alkylaluminum and Amines (1,2). NMR spectra of a solution of Me_3AlNH_3 (≈ 0.1 M) in D_8 -toluene show a steady upfield movement of the N-H proton signal as temperature decreases from 80 to -90°C . An opposite shift would be expected for increased complexation as temperature decreases. Instead, this is attributed to the formation of a weak complex between the aromatic π cloud and the relatively positive N-H protons, causing a shielding effect.³⁴ This complexation also explains the adduct's much higher solubility in aromatic solvents than in alkanes.

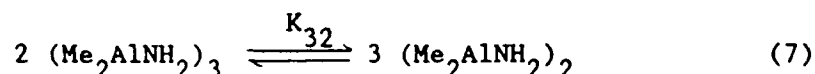
Me_3AlNH_3 and $(\text{Me}_3\text{Al})_2$ (≈ 0.1 M each in D_6 -benzene solution, 10 - 80°C) show two separate methyl resonances at -0.74 and -0.35 ppm, respectively, indicating that exchange is slow on the NMR time scale. In contrast, for a solution of Me_3AlNH_3 (≈ 0.1 M) in excess NH_3 (≈ 0.3 M), only one N-H signal is seen; exchange must be rapid on the NMR time scale. Analogous solutions containing $\text{Me}_3\text{AlNH}_2\text{Me}$ and excess NH_2Me show only one N-H and one set of N-Me peaks, even when cooled to -90°C in D_8 -toluene, also demonstrating rapid exchange. Since the exchange of methyl groups on nitrogen is improbable, we conclude that whole-molecule exchange of coordinated amine is rapid down to -90°C . Below *ca.* -30°C coupling between the N-H and N-Me appears in the presence of excess amine, indicating that proton exchange becomes slow on the NMR time scale under these conditions. This indicates that whole-molecule amine exchange is more facile than proton exchange.

N-H shifts are similar to those for the ammonia complex, indicating similar π -complexes and hydrogen bonding.

Since exchange is much more rapid in the presence of excess amine than with excess $(\text{Me}_3\text{Al})_2$, the process is probably associative, as proposed by Mole.³⁵

C. Monomer - Dimer - Trimer Equilibrium (7). The small peak 0.1 ppm downfield from the $(\text{Me}_2\text{AlNH}_2)_3$ methyl peak (cf. Figure 1 inset) was noted to vary in relative height with total amide concentration, and to increase reversibly with temperature, indicating the species responsible to be in equilibrium with the trimer. Solutions of varying total $(\text{Me}_2\text{AlNH}_2)_x$ concentration were prepared, the peak heights measured, and the equilibrium constant for the reaction

Figure 1



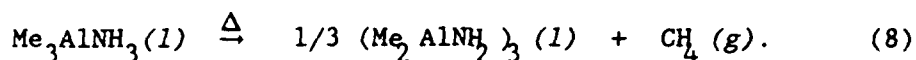
was computed. (The small value of K_{32} precluded its determination by molecular weight measurements.) Determination of K_{32} at temperatures 40 - 80 °C allowed calculation of ΔH . K_{32} is 2×10^{-5} at 80 °C; ΔH is 38.4 kJ for the reaction as written. Equilibration is rapid compared with methane loss from the adduct, which supports the assumption of rapid equilibration made below in the rate law interpretation. Details are reported elsewhere.³⁶

Mixing of $(\text{Me}_2\text{AlNH}_2)_3$ and $(\text{Et}_2\text{AlNH}_2)_3$ (≈ 0.1 M each in D_6 -benzene, less than 30 min at ambient temperature) produces only partial scrambling, i.e. Et_2Al and Me_2Al units remain intact, and no EtMeAl units are produced (Figure 2A). Heating to 80 °C for an hour still produces no EtMeAl units. This is consistent with dissociation

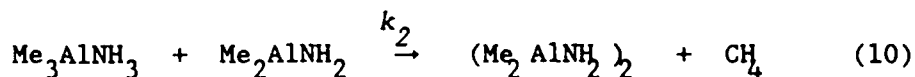
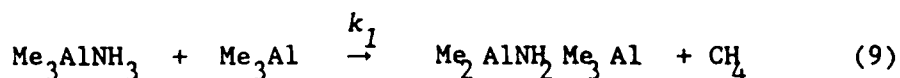
into Et_2AlNH_2 and Me_2AlNH_2 monomers which randomly combine. As this exchange is also faster than methane loss from the adduct, the assumption of rapid equilibrium made below is further supported.

There are, of course, other mechanisms which can account for these exchanges. Our principal justification for assuming the presence of Me_2AlNH_2 monomers is the rate law below (D). It is interesting to note that the analogous Me_2BNH_2 is a dimer below 30 °C but a monomer at higher temperatures.³⁷

D. Decomposition (3, 4, 5). DSC measurements show that $\Delta H = -82.2$ kJ/mole for methane loss from the adduct:



Our experimental rate law suggests that this decomposition process takes place via two routes, one catalyzed by free Me_3Al and one by monomeric Me_2AlNH_2 .

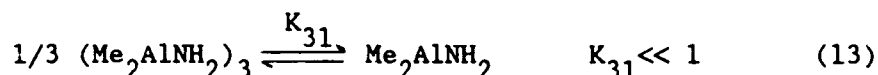
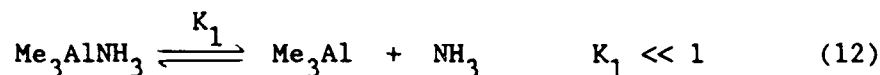


The rate law for this two - path mechanism is

$$R = -d[\text{Me}_3\text{AlNH}_3]/dt =$$

$$k_1 [\text{Me}_3\text{AlNH}_3] [\text{Me}_3\text{Al}] + k_2 [\text{Me}_3\text{AlNH}_3] [\text{Me}_2\text{AlNH}_2]. \quad (11)$$

If we assume the rapid dissociation equilibria



the rate law then becomes

$$R = k_1 \sqrt{K_1} [\text{Me}_3\text{AlNH}_3]^{3/2} + k_2 K_{31} [\text{Me}_3\text{AlNH}_3] [(\text{Me}_2\text{AlNH}_2)_3]^{1/3} \quad (14)$$

Plots of $\ln(\text{Fr})$ vs. time for solutions containing varied initial concentrations of Me_3AlNH_3 and $(\text{Me}_2\text{AlNH}_2)_3$ are shown in Figures 3 and 4. Solid lines show the results obtained from the proposed rate law (eq. 14), with $k_1 \sqrt{K_1} = 5.5 \times 10^{-4}$ and $k_2 K_{31} = 1.5 \times 10^{-3}$.

Figure 3
Figure 4

Attempts to fit the data to single term rate laws failed, demonstrating that the reaction is not simply n-order in reactant. Rate laws containing several terms of different power in reactant, appropriate to a multipath but uncatalyzed mechanism also fail to fit our results.

The observed value of 3/2 for the first exponent in equation (14) eliminates both equation (12) as a rate-determining step (an exponent of 1 would be required) and $(\text{Me}_3\text{Al})_2$ as catalyst (requires an exponent of 2). The experimental value of 1/3 for the second exponent in equation (14) eliminates equation (13) as rate-determining (1 required) as well as $(\text{Me}_2\text{AlNH}_2)_{2\text{or}3}$, either in cyclic or ring - opened forms, as catalyst (2/3 or 1 required).

The extent of Me_3AlNH_3 dissociation must be small, as Me_3AlNH_3 in solution shows no sign of a peak due to free $(\text{Me}_3\text{Al})_2$. A peak 10% of the principal peak in 0.01 M solution would have been easily

discernible. This yields $K_1 < 10^{-4}$ at 20 °C. ΔH^\ddagger for dissociation must of course equal or exceed 93 kJ/mole.

E. Me_2AlNH_2 - Catalyzed decomposition (3). We consider the decomposition of a solution of Me_3AlNH_3 , and rearrange the rate law (eq. (14)) to

$$R = (k_1 \sqrt{K_1} [\text{Me}_3\text{AlNH}_3]^{1/2} + k_2 K_{31} [(\text{Me}_2\text{AlNH}_2)_3]^{1/3}) [\text{Me}_3\text{AlNH}_3] \quad (15)$$

In the later portion of the decomposition the reaction is dominated by the Me_2AlNH_2 - catalyzed pathway, as $k_1 \sqrt{K_1}$ and $[\text{Me}_3\text{AlNH}_3]$ are both small. The first term in brackets becomes insignificant, and the rate law in this region becomes

$$R \approx k_2 K_{31} [(\text{Me}_2\text{AlNH}_2)_3]^{1/3} [\text{Me}_3\text{AlNH}_3] - k_{ps} [\text{Me}_3\text{AlNH}_3] \quad (16)$$

Recognizing that in this region decomposition is largely complete, $[(\text{Me}_2\text{AlNH}_2)_3]$ is approximately equal to the initial $[(\text{Me}_2\text{AlNH}_2)_3]$ plus one-third the initial $[\text{Me}_3\text{AlNH}_3]$, and varies but little with time. The reaction thus becomes pseudo-first order in Me_3AlNH_3 with

$$k_{ps} = k_2 K_{31} (1/3 [\text{Me}_3\text{AlNH}_3]_{\text{init}} + [(\text{Me}_2\text{AlNH}_2)_3]_{\text{init}})^{1/3} \quad (17)$$

This implies that the plots of $\ln(\text{Fr})$ vs. time should become linear in the latter portion, as decomposition is largely complete. The limiting slope (k_{ps}) should vary with the initial concentrations according to eq. (17). This prediction is confirmed in Figure 5. A

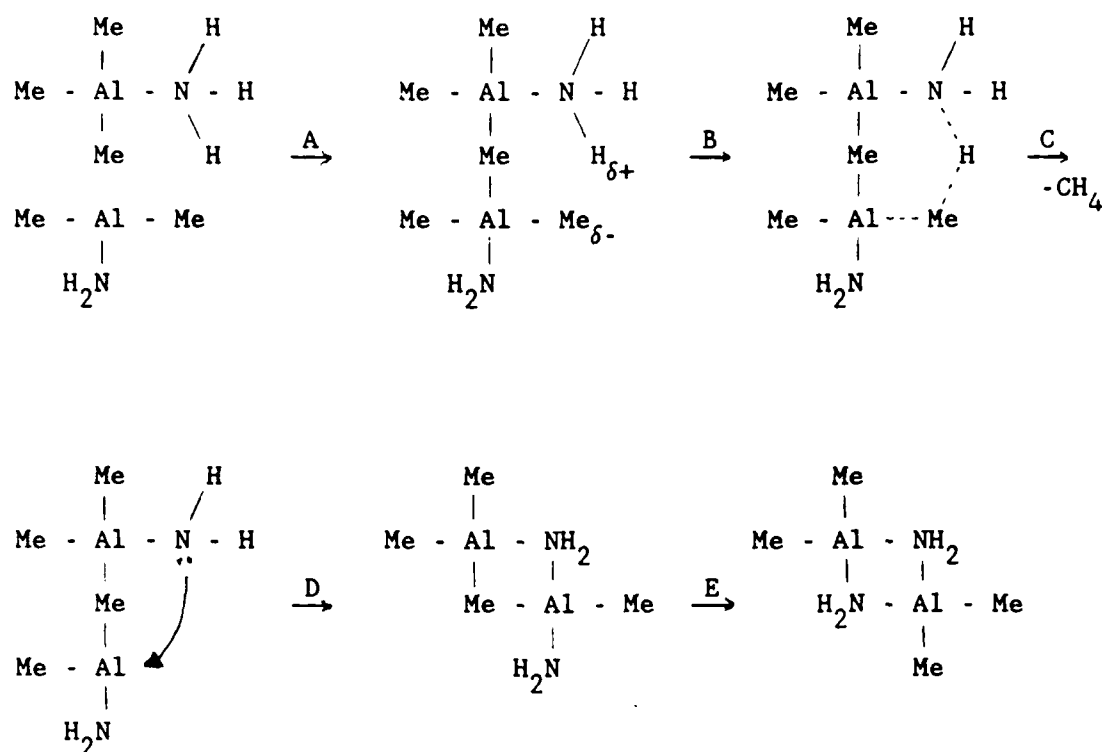
Figure 5

series of solutions with varying initial $[\text{Me}_3\text{AlNH}_3]$ and $[(\text{Me}_2\text{AlNH}_2)_3]$ was prepared and their decompositions monitored. k_{ps} is seen to be linear in the quantity $(1/3 [\text{Me}_3\text{AlNH}_3]_{\text{init}} + [(\text{Me}_2\text{AlNH}_2)_3]_{\text{init}})^{1/3}$.

Me_3AlNH_3 (0.2 M) was decomposed in D_6 -benzene at various temperatures. A plot of $\ln k_{\text{ps}}$ vs. $1/T$ (Figure 6) gave ΔH^\ddagger of 92.8 ± 1.2 kJ/mole. Identical measurements using Me_3AlND_3 gave ΔH^\ddagger of 109 ± 2.5 kJ/mole. Direct comparison of solutions of identical concentration gave a deuterium isotope effect of 8.8 at 67.2°C . Substitution of D for H would not be expected to alter K_{31} significantly in aromatic solvents; these results thus indicate substantial N-H bond breaking at the transition state.

The rate law implies that the transition state for the Me_2AlNH_2 - catalyzed pathway contains one Me_2AlNH_2 and one Me_3AlNH_3 . The isotope effect suggests that N-H bond breaking is important.

We postulate that the Me_2AlNH_2 - catalyzed methane loss begins with formation of a methyl bridge between the adduct methyl group and the empty p_z orbital of the Me_2AlNH_2 (A). The highly acidic N-H then attacks the nearby electron - rich methyl group which departs as methane (B, C). The nitrogen lone pair forms a bond with the empty aluminum orbital yielding a methyl-bridged ring (D), which then rearranges to the more stable amino-bridged form (E).



Mechanisms involving initial attack of the catalyst on the adduct nitrogen are less plausible, as this nitrogen bears a significant positive charge and is therefore less attractive to the Lewis acid catalyst.

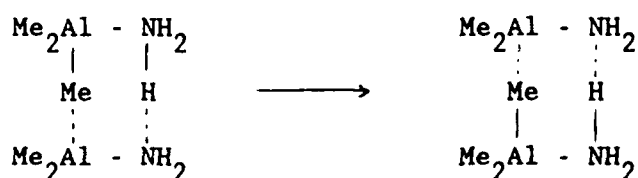
Excess ammonia slows the Me_2AlNH_2 - catalyzed reaction by a factor of up to 3 (Figure 7). ΔH^\ddagger appears to increase slightly (from 92.8 to 98.4 kJ/mole) in going from no excess NH_3 to approximately 5-fold excess. This could be due to H-bonding between the very positive adduct N-H protons and the ammonia lone pair, or because the excess NH_3 forms a complex with the monomeric amide catalyst.

Figure 7

Using DSC measurements an activation enthalpy of 174 kJ/mole and order = 1 were found for the decomposition of the neat liquid Me_3AlNH_3 . This should correspond to the Me_2AlNH_2 - catalyzed decomposition. The substantially larger activation enthalpy obtained

compared to the value in benzene solution could be related to the difference in the reaction medium; however, the DSC values in this case are subject to substantial positive errors due to overlap of both the endothermic Me_3AlNH_3 fusion with the early part of the decomposition, and the exothermic $(\text{Me}_2\text{AlNH}_2)_3$ solidification with the latter part (Figure 8). We therefore have less confidence in this determination.

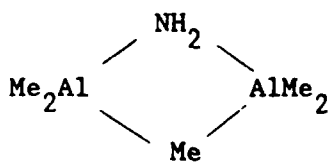
F. Alkyl Exchange. If a solution containing Me_3AlND_3 and $(\text{Me}_2\text{AlND}_2)_3$ in D_8 -toluene is heated to 110°C , the methyl resonances broaden and begin to coalesce, demonstrating fast exchange - much faster than the loss of CH_3D . (The deuterated compound and toluene solvent are required to slow the decomposition and to allow a higher temperature.) A natural modification of the previous mechanism explains this result. Rotation of the Me_2AlNH_2 about the methyl bridge leads to a slightly different geometry. H^+ transfer and subsequent dissociation yields simultaneous methyl and hydrogen exchange, in effect interchanging the identities of adduct and amide.



Electrostatic interaction of the adduct's positive N-H with the N atom would be expected to make this geometry more favorable than that resulting in methane elimination. Thus methyl (and H or D) exchange would occur more rapidly than methane loss. This rapid exchange further supports the assignment of H^+ transfer, rather than methyl bridge formation, as the rate-determining step.

In addition, when Me_3AlNH_3 is added to $(\text{Et}_2\text{AlNH}_2)_3$ in D_6 -benzene, ethane is rapidly evolved, and mixed trimers with complete alkyl scrambling result (compare Figures 2A and 2B). As noted above in C, mixing the $(\text{Me}_2\text{AlNH}_2)_3$ and $(\text{Et}_2\text{AlNH}_2)_3$ does not scramble the alkyl groups; the scrambling therefore occurs before or during alkane loss. Combining the previous mechanisms explains this.

G. Me_3Al - Catalyzed Decomposition (5, 6). When Me_3AlNH_3 is decomposed in the presence of small amounts of $(\text{Me}_3\text{Al})_2$ the reaction is slowed dramatically, due to suppression of the more efficient Me_2AlNH_2 - catalyzed pathway. (Note the high value of the initial point in Figure 9, where $[(\text{Me}_3\text{Al})_2] = 0$, compared with subsequent points.) An increase in the amount of $(\text{Me}_3\text{Al})_2$ then gradually increases the rate, now due only to the less efficient Me_3Al - catalyzed route, and shortens the time required for the Me_2AlNH_2 - catalyzed decomposition rate to become appreciable. This sharp drop followed by a gradual rise is shown in Figure 9. This is probably due to trapping of Me_2AlNH_2 to form the metastable methyl-bridged species as the kinetic product



which then gradually disproportionates into $(\text{Me}_2\text{AlNH}_2)_3$ and $(\text{Me}_3\text{Al})_2$.

The ^1H NMR spectrum of a sample of Me_3AlNH_3 which has been partially decomposed in the presence of $(\text{Me}_3\text{Al})_2$ at 75°C , then cooled to 50°C , is shown in Figure 10. At the temperature of decomposition, the species we believe to be $(\mu\text{-NH}_2)(\mu\text{-Me})\text{Al}_2\text{Me}_4$ resonates at the same

frequency as the Me_3AlNH_3 . However, at lower temperatures, its resonance moves downfield and appears as a separate peak between those of $(\text{Me}_3\text{Al})_2$ and Me_3AlNH_3 . As the decomposition proceeds, the peak attributed to $(\mu\text{NH}_2)(\mu\text{Me})\text{Al}_2\text{Me}_4$ increases, then rapidly decreases. As Me_3AlNH_3 decomposition nears completion this peak no longer appears. The product peak initially grows very slowly as it is trapped as the intermediate, then rapidly as the intermediate decomposes.

This bridged species does not form when the decomposition proceeds in the absence of excess $(\text{Me}_3\text{Al})_2$, justifying its neglect in the rate law in D. Heating a mixture of $(\text{Me}_3\text{Al})_2$ and $(\text{Me}_2\text{AlNH}_2)_3$ also does not generate detectable amounts of this species, in agreement with the conclusions of Ziegler³⁸ and Schram³⁹ that $(\mu\text{-NR}')(\mu\text{-R})\text{Al}_2\text{R}_4$ are not stable if R' is aliphatic. Analogous species with phenyl or trimethylsilyl R' groups are stable.⁴¹⁻⁴⁴

A solution containing 0.0824 M Me_3AlNH_3 and 0.124 M $(\text{Me}_3\text{Al})_2$ to suppress the Me_2AlNH_2 - catalyzed pathway was prepared. The initial rate of decomposition was determined at temperatures between 35 and 55 °C as described in the Experimental section. A plot of $\ln(\text{Slope})$ vs. $1/T$ gave $\Delta H^\ddagger = 113 \pm 7$ kJ/mole.

An identical solution, prepared with Me_3AlND_3 in place of Me_3AlNH_3 was also decomposed at 55 °C. The deuterium isotope effect was $R_H/R_D = 5.5$. This implies N-H bond breaking is significant at this transition state also.

We propose that Me_3Al - catalyzed decomposition of Me_3AlNH_3 proceeds via a path similar to that for Me_2AlNH_2 catalysis. The only difference is that the methyl-bridged ring formed in step D cannot rearrange to a more stable ring, because a methyl group occupies the position of the exocyclic NH_2 , but instead disproportionates to

$(\text{Me}_3\text{Al})_2$ and $(\text{Me}_2\text{AlNH}_2)_3$. This mechanism is consistent with the rate law, which requires a monomeric Me_3Al catalysis, the observed isotope effect, and the metastable product formed.

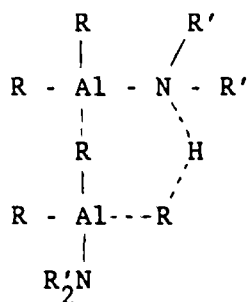
The observed ΔH^\ddagger values are the sum of ΔH for production of the monomeric catalytic species and ΔH^\ddagger for the actual methane loss step. For the Me_3Al - catalyzed reaction the ΔH^\ddagger for the decomposition step is therefore $113 - 81.2$ or 31 kJ/mole.

The analogous ΔH for production of monomeric Me_2AlNH_2 is unavailable. Since the NH_2 bridge is stronger than a methyl bridge, it is reasonable to expect it to be higher than 81.2 kJ/mole. Subtraction of this quantity from the observed 92.8 kJ/mole yields a ΔH^\ddagger for the Me_2AlNH_2 - catalyzed step of less than 12 kJ/mole. This is plausible, as replacing a methyl group on the catalyst's Al with an NH_2 would make the catalyst a stronger Lewis acid, strengthen the Al-Me-Al bridge and stabilize the transition state.

Computation of apparent ΔS^\ddagger values, which would represent the sum of ΔS for monomeric catalyst generation and ΔS^\ddagger for transition state formation, serves little purpose in view of the unknown value of the transmission coefficient required.

H. Uncatalyzed Decomposition (7). Extrapolating the data in Figure 9 to $[(\text{Me}_3\text{Al})_2] = 0$ yields an intercept near zero. This corresponds to the rate of unimolecular Me_3AlNH_3 methane loss, assuming suppression of the Me_2AlNH_2 - catalyzed pathway. Although uncatalyzed methane loss for this compound cannot be ruled out, its rate is sufficiently low that we cannot observe it.

I. Comparisons With Earlier Results. For the purposes of our discussion, we write the transition state for the autocatalytic alkane loss as shown below



and consider the effect of altering the various groups on the rate of RH elimination, assuming that a similar mechanism to that proposed herein for Me_3AlNH_3 applies in all these cases. This is clearly an oversimplification of a complex set of observations; however, it makes possible the organization and rationalization of a substantial body of otherwise uncorrelated experimental information.

Variations at the Aluminum.

(1) Changing R from methyl to ethyl, propyl, or isobutyl speeds alkane loss to such an extent that the corresponding R_3AlNH_3 adducts cannot be readily isolated.¹⁷ This could arise from either a decreased Al-C bond strength in these compounds relative to $\text{R} = \text{Me}$ ⁴⁵, which would facilitate the breaking of the aluminum - alkyl bond at the transition state, or from a higher concentration of the corresponding R_2AlNH_2 monomers. In the latter case, we have demonstrated that the increased steric interaction causes the corresponding dialkylaluminum amide trimers to dissociate to dimers to a much greater extent than the methyl trimer.³⁶ It is reasonable to suppose that there is a greater R_2AlNH_2 monomer concentration for these compounds as well, leading to more efficient catalysis.

(2) If R is H instead of Me the reaction is speeded enormously.⁴⁶ This may be due to the much lower steric requirements of the H atom, facilitating approach by the N-H at the transition

state.

(3) Replacement of methyl by *t*-butyl slows the alkane loss dramatically.¹⁴ This is probably due both to the poor ability of *t*-butyl to bridge aluminum atoms and to the steric inhibition of the approach of the N-H hydrogen to the central carbon of the *t*-butyl group.

(4) The loss of benzene when phenyl groups are on the aluminum is more difficult than methane loss⁴⁷, in spite of the excellent bridging ability of the phenyl group. The larger expected Al-phenyl bond strength compared with Al-alkyl bond strengths would explain this⁴⁵.

(5) Replacement of one R group by a chlorine also slows the reaction.⁴⁸ Electron withdrawal by the chlorine would make the carbon attached to the aluminum less electron-rich and less attractive to the proton being transferred.

Variations at the Nitrogen.

The literature data is much more extensive for Et₃Al adducts. Comparisons below are made using the triethyl derivatives.

(1) Changing R' from hydrogen to methyl or *t*-butyl slows the reaction, most likely due to crowding at the transition state as suggested by Mole and Jeffery.⁴⁹ The lower acidity of the alkyl amine would also slow the proton transfer step.

(2) If R' is phenyl, the reaction rate is increased compared to *t*-butyl (similar steric requirements), and even when compared with hydrogen.⁵⁰ We ascribe this to the greater acidity of aryl amines, facilitating H⁺ transfer at the transition state.

(3) The very rapid reactions which occur when alcohols are used in place of amines is also attributable to their greater acidity⁵¹.

Acknowledgments

$[\text{Me}_2\text{AlNH}_2]_3$ and $[\text{Me}_2\text{AlNHMe}]_3$ were prepared by Wei Lee; $[(\text{Et}_2\text{AlNH}_2)_3]$ by Christopher Warren. Dr. Herbert Schwartz assisted with NMR measurements. We thank Drs. Corinna L. Czekaj, Johannes F. Coetzee and Raymond Borkowski for helpful discussions, Chris Whitmarsh for assistance with the DSC measurements, and the reviewers for incisive criticism.

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Figure Captions.

Scheme 1. A summary of the decomposition of Me_3AlNH_3 .

Figure 1. ^1H NMR spectrum of partially decomposed Me_3AlNH_3 in D_6 -benzene. Inset: methyl region as decomposition proceeds.

Assignments: Me_3AlNH_3 A - N-H, B - Me; $(\text{Me}_2\text{AlNH}_2)_3$ C - N-H, D - Me; methane - E; $(\text{Me}_2\text{AlNH}_2)$ F - Me; impurity - G.

Figure 2A. ^1H NMR spectrum of $(\text{Et}_2\text{AlNH}_2)_3$ and $(\text{Me}_2\text{AlNH}_2)_3$ mixture in D_6 -benzene after heating for 10 minutes at 80°C . Four species, $(\text{Et}_2\text{AlNH}_2)_3$, $(\text{Et}_2\text{AlNH}_2)_2\text{Me}_2\text{AlNH}_2$, $\text{Et}_2\text{AlNH}_2(\text{Me}_2\text{AlNH}_2)_2$, and $(\text{Me}_2\text{AlNH}_2)_3$, give three distinct and resolved methyl and ethyl environments.

Figure 2B. ^1H NMR spectrum of $(\text{Et}_2\text{AlNH}_2)_3$ and Me_3AlNH_3 mixture in D_6 -benzene after heating for 10 minutes at 80°C . Alkyl scrambling yields the mixture of products $((\text{Me},\text{Et})_2\text{AlNH}_2)_3$ containing 9 different species whose resonances are not resolved, along with ethane and a very small amount of methane.

Figure 3. Plots of $\ln(\text{fraction remaining})$ [$\ln(\text{Fr})$] vs. time at 61.5°C for solutions containing varied initial concentrations of Me_3AlNH_3 and $(\text{Me}_2\text{AlNH}_2)_3$, respectively; Δ , 0.0214 M, 0.002 M; \circ , 0.0414 M, 0.0007 M; \bullet , 0.0614 M, 0.0034 M; Δ , 0.11 M, 0.0046 M; ∇ , 0.2117 M, 0.0207 M. The solid lines were computed using the proposed rate law.

Figure 4. Plots of $\ln(\text{Fr})$ vs. time at 61.5°C for solutions containing 0.0565 M Me_3AlNH_3 and varied concentrations of $(\text{Me}_2\text{AlNH}_2)_3$; ∇ , 0.0057 M; \circ , 0.0251 M; Δ , 0.0592 M; \bullet , 0.182 M. The solid lines

were computed using the proposed rate law.

Figure 5. Test for pseudo-first order behavior. For Δ the initial concentrations were those of Figure 3. For ∇ , Figure 4.

Figure 6. Determination of ΔH^\ddagger for the catalyzed methane loss from Me_3AlNH_3 . k_{ps} is the pseudo-first order rate constant. All solutions were initially 0.2 M in Me_3AlNH_3 (Δ) or Me_3AlND_3 (∇).

Figure 7. Influence of NH_3 on the Me_2AlNH_2 - catalyzed methane loss from Me_3AlNH_3 at 51.7 °C. Initial $[\text{Me}_3\text{AlNH}_3]$ ca. 0.1 M.

Figure 8. DSC for Me_3AlNH_3 heated at 2 °C/minute in a sealed stainless steel pan.

Figure 9. Influence of $[(\text{Me}_3\text{Al})_2]$ on the initial rate of 0.081 M Me_3AlNH_3 decomposition at 55 °C.

Figure 10. ^1H NMR spectrum of a solution of Me_3AlNH_3 and $(\text{Me}_3\text{Al})_2$ in D_6 -benzene, approximately half decomposed at 75 °C, then cooled to 50 °C.